

## PATENT ABSTRACTS OF JAPAN

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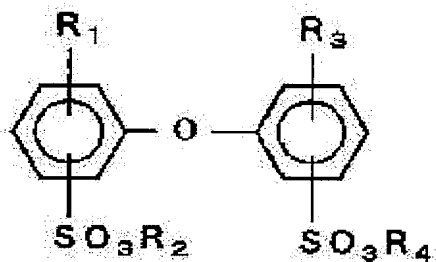
(71)Applicant : SUMITOMO BAKELITE CO  
LTD

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(72)Inventor : MAKABE HIROAKI  
BANBA TOSHIO  
HIRANO TAKASHI(54) DEVELOPING SOLUTION FOR POSITIVE PHOTSENSITIVE RESIN  
COMPOSITION AND PATTERN FORMING METHOD USING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance sensitivity and film etching resistance, and to prevent occurrence of scum in a pattern processing stage and to enhance resolution by using an anionic surfactant and an aqueous alkaline solution containing an extremely small amount of chlorine.



SOLUTION: The developing solution for positive photosensitive resin composition to be used contains the anionic surfactant and the aqueous alkaline solution containing an extremely small amount of chlorine, and the preferable anionic surfactant has a structure represented by the formula in which each of R1

and R3 is an H atom or a 7-17C alkyl or alkoxy group and at least one of them is a 7-17C alkyl or a alkoxy group; and each of R2 and R4 is an Na atom or an ammonium group or one selected from primary-quarternary ammonium groups. A content of the

anionic surfactant is 0.1-10 weight % and a concentration of chlorine is 2-200 ppm.

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#### CLAIMS

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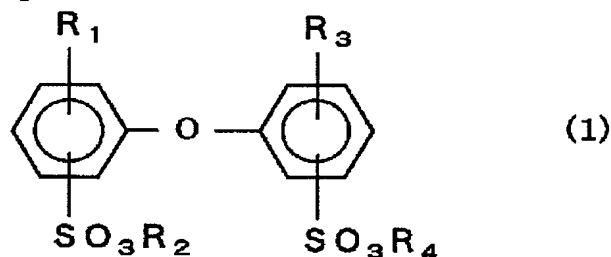
[Claim(s)]

[Claim 1] An anionic surface active agent, the developer for positive type  
photopolymer constituents characterized by consisting of an alkaline water solution  
containing chlorine.

[Claim 2] The developer for positive type photopolymer constituents according to

claim 1 in which this anionic surface active agent is shown by the following formula (1).

[Formula 1]



(式中、 $R_1$ ,  $R_3$ は水素原子または炭素数7～17のアルキル基またはアルコキシ基を表し、 $R_1$ ,  $R_3$ の内、少なくとも一つは炭素数7～17のアルキル基またはアルコキシ基を示す。

$R_2$ ,  $R_4$ はそれぞれナトリウム原子、アンモニウム基、第1～4級アンモニウム基の内から選ばれた1つを示す。)

[Claim 3] The developer for positive type photopolymer constituents according to claim 1 or 2 whose content of this anionic surface active agent is 0.1 – 10 % of the weight.

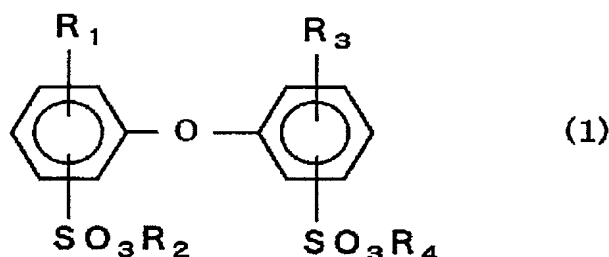
[Claim 4] The developer for positive type photopolymer constituents according to claim 1, 2, or 3 whose concentration of this chlorine is 2–200 ppm.

[Claim 5] The developer for positive type photopolymer constituents according to claim 1 with which this positive type photopolymer constituent consists of a polyamide and a diazo quinone compound.

[Claim 6] The pattern formation approach of the positive type photopolymer constituent which carries out dissolution removal of the exposure section with the developer which consists of an anionic surfactant and an alkaline water solution containing chlorine after applying a positive type photopolymer constituent to a substrate etc. and performing prebaking and an optical exposure, and is characterized by obtaining a pattern.

[Claim 7] The pattern formation approach of a positive type photopolymer constituent according to claim 6 by which this anionic surface active agent is shown by the following formula (1).

[Formula 2]



(式中、 $R_1$ ,  $R_3$ は水素原子または炭素数7～17のアルキル基またはアルコキシ基を表し、 $R_1$ ,  $R_3$ の内、少なくとも一つは炭素数7～17のアルキル基またはアルコキシ基を示す。

$R_2$ ,  $R_4$ はそれぞれナトリウム原子、アンモニウム基、第1～4級アンモニウム基の内から選ばれた1つを示す。)

[Claim 8] The pattern formation approach of a positive type photopolymer constituent according to claim 6 or 7 that the content of this anionic surface active agent is 0.1 – 10 % of the weight.

[Claim 9] The pattern formation approach of a positive type photopolymer constituent according to claim 6, 7, or 8 that the concentration of this chlorine is 2–200 ppm.

[Claim 10] The pattern formation approach of a positive type photopolymer constituent according to claim 6 that this positive type photopolymer constituent consists of a polyamide and a diazo quinone compound.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention does not have the development remainder and

relates to the pattern formation approach of the developer for photopolymer constituents for obtaining the pattern of high resolution, and the photopolymer constituent using it.

[0002]

[Description of the Prior Art] In recent years, in semi-conductor industry, photopolymers, such as a photoresist and photosensitive polyimide, are overly used abundantly at the insulator layer and protective coat in creation of a detailed circuit or the required packages of processing, such as IC and LSI. The description of a photopolymer is the point that a highly precise resin pattern can be obtained with comparatively simple equipment. Since especially the photoresist of the positive type which used as the base the phenol novolak resin which used the diazo quinone etc. for the sensitization agent does not start swelling at the time of development, formation of the pattern excellent in resolution is possible for it. Moreover, since it has many descriptions referred to as excelling also in a safety aspect since a developer is an alkaline water solution, it is used abundantly at manufacture of the detailed circuit of the above-mentioned semi-conductor etc.

[0003] On the other hand, the photosensitive heat resistant resin of the positive type which has the descriptions of high resolution or a developer, such as nonpolluting, also in photosensitive heat resistant resin like the photosensitive polyimide used for the insulator layer and protective coat of a semi-conductor attracts attention as the insulator layer and the resin for protective coats of the semi-conductor which it was developed like the photoresist (for example, JP,64-60630,A, JP,1-46862,B, etc.), and was integrated highly.

[0004] Most positive type photopolymer constituents consist of combining the above diazo quinone compounds with an alkali fusibility polymer as a sensitization agent. In an unexposed part, although these diazo quinone compound is insoluble in an alkaline water solution, it becomes meltable in a lifting alkalinity water solution about a chemical change by exposure. Therefore, creation of the paint film pattern of only an unexposed part is attained by using this exposure / unexposed solubility difference, and removing the exposure section in an alkaline water solution.

[0005] Generally as an ant potash nature water solution used as a developer, it is the water solution of tetramethylammonium hydroxide (henceforth TMAH). Although negatives could be developed good in the water solution of this TMAH when the photoresist which used usual phenol novolak resin as the base was developed, in the case of the photopolymer constituent which used the poly benzooxazole precursor as shown in JP,1-46862,B as the base, for example, the development remainder (Society

for Cutting Up Men) occurred in the exposure section which dissolves completely and should originally be removed, and there was a fault that resolution worsened.

[0006] \*\* known well — as a property of evaluating these photopolymers, contrast (how is the difference of the solubility to the developer of the exposure section and an unexposed part large?) is raised like with sensibility (how can a pattern be formed with little exposure energy?), and resolution (how can the pattern of a detailed configuration be formed?). If its attention is paid to this contrast here, since the polymer itself which serves as the base in this sensitization system is meltable in an alkali solution irrespective of exposure/unexposed one, it will also dissolve an unexposed part at the time of development. Therefore, in the development which used the conventional alkali developer, the thickness of an unexposed part decreased and good contrast was not acquired.

[0007] In order to improve this fault, soluble modifiers, such as a heterocyclic compound and a cyclic anhydride, are added in a photopolymer constituent, and the approach of controlling the solubility of resin is learned (JP,48-12242,B, JP,56-30850,B). However, as for these additives, after development remains into resin. Therefore, the thermal resistance of a photopolymer, the machine engine performance, etc. fell with these additives, and made difficult use to applications, such as a semi-conductor insulator layer, for the photopolymer. Moreover, although the rate of film decrease improved when the developer for photopolymers as shown in JP,3-104053,A was used, there was a problem to which sensibility and resolution fall.

[0008]

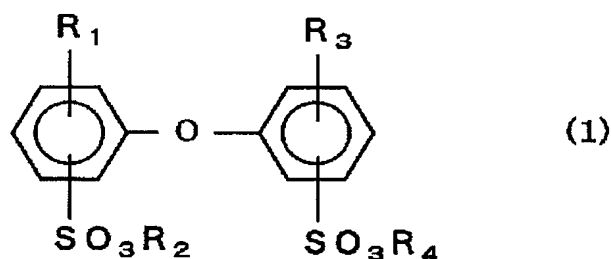
[Problem(s) to be Solved by the Invention] This invention abolishes Society for Cutting Up Men in a pattern processing process, and it not only excels in sensibility and the rate of film decrease, but it offers the pattern formation approach of the developer for photopolymer constituents with which high resolution is obtained, and a photopolymer constituent.

[0009]

[Means for Solving the Problem] This invention is a developer for positive type photopolymer constituents which consists of an anionic surface active agent and an alkaline water solution containing the chlorine of ultralow volume, and is the pattern formation approach of the positive type photopolymer constituent using it.

[0010] Furthermore, as an anionic surfactant, the thing of the structure shown by the following formula (1) is desirable.

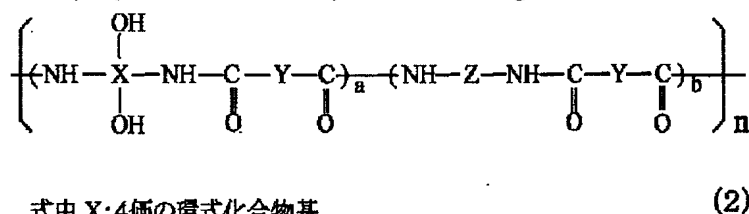
[Formula 3]



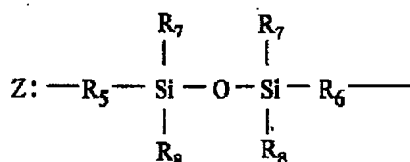
(式中、 $\text{R}_1, \text{R}_3$ は水素原子または炭素数7～17のアルキル基またはアルコキシ基を表し、 $\text{R}_1, \text{R}_3$ の内、少なくとも一つは炭素数7～17のアルキル基またはアルコキシ基を示す。

$\text{R}_2, \text{R}_4$ はそれぞれナトリウム原子、アンモニウム基、第1～4級アンモニウム基の内から選ばれた1つを示す。)

The polyamide shown by the following formula (2), [Formula 4]



式中 X:4価の環式化合物基  
Y:2価の環式化合物基



( $\text{R}_5, \text{R}_6$ :2価の有機基、 $\text{R}_7, \text{R}_8$ :1価の有機基)

a、b はモル分率を示し、 $a+b=100$ モル%  
 $a=60.0 \sim 100.0$ モル%  
 $b=0 \sim 40.0$ モル%  
 $n=2 \sim 500$

After prebaking by applying to a substrate etc. the positive type photopolymer constituent which consists of a diazo quinone compound and performing an optical exposure, it is the pattern formation approach of a photopolymer constituent of carrying out dissolution removal of the exposure section with the developer which

consists of an anionic surfactant and an alkaline water solution containing the chlorine of ultralow volume, and obtaining a pattern. Moreover, the content of this anionic surfactant is 0.1 – 10 % of the weight, and the concentration of this chlorine is 2–200 ppm.

[0011]

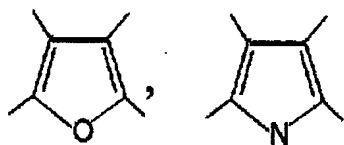
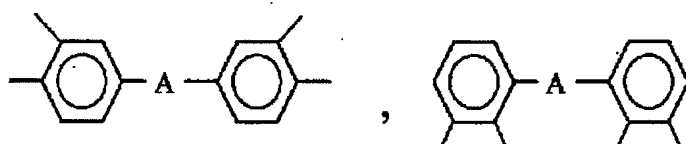
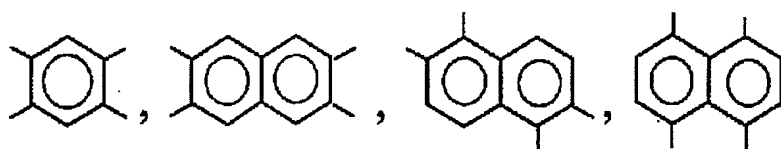
[Embodiment of the Invention] The polyamide of a formula (2) consists of dicarboxylic acid which has the structure of the bis-aminophenol and Y which have the structure of X, if this polyamide is heated at about 300–400 degrees C, a ring closure will be carried out, and it changes to heat resistant resin called the poly benzooxazole.

Generally a positive type photopolymer constituent develops negatives in an alkali water solution. For example, since the photoresist has the phenolic hydroxyl group in the phenol novolak resin of the base, the development of it is attained. Although the development also of the positive type photopolymer which used as the base the polyamide similarly expressed with a formula (2) is attained with the phenolic hydroxyl group in the bis-aminophenol which has the structure of X, from the photoresist which used phenol novolak resin as the base, the development nature is inferior, Society for Cutting Up Men is generated in the exposure section, and resolution worsens.

[0012] This is considered because a hydroxyl group does not spread on an amine component to the one benzene ring in the polyamide shown in a formula (2) to the phenol novolak resin with which one hydroxyl group is contained. Since the solubility of resin becomes still lower, many Society for Cutting Up Men generates the polyamide replaced with the silicone diamine which has the structure of Z of a formula (2) for adhesion amelioration of a part of bis-aminophenol which has the structure of X etc., and resolution gets very bad. However, if it is processed in the alkali water solution containing the anionic surfactant of this invention, this Society for Cutting Up Men will not be generated at all. Although it is not clear about a cause, it thinks for the compatibility of resin and a developer to improve with an anionic surfactant.

[0013] X of the formula (2) which is the polyamide of this invention is [Formula 5].

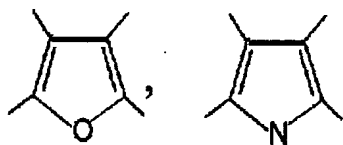
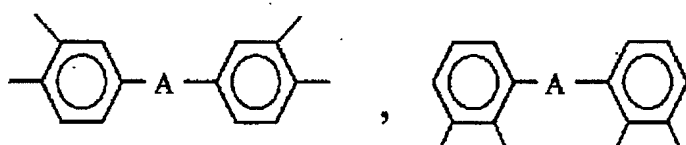
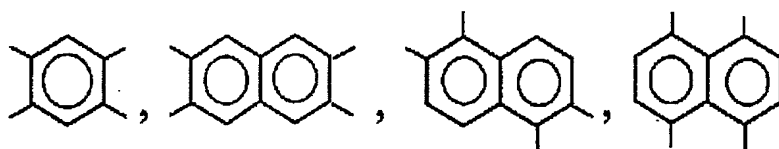




(式中A:  $-\text{CH}_2-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  
 $-\text{NHCO}-$ ,  $-\text{C}(\text{CF}_3)_2-$ )

\*\*\*\*\* -- although -- it is not limited to these.

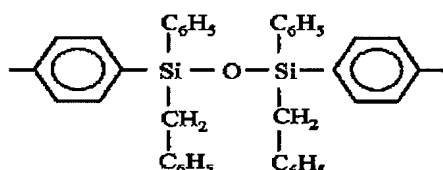
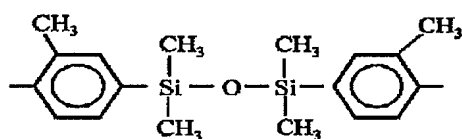
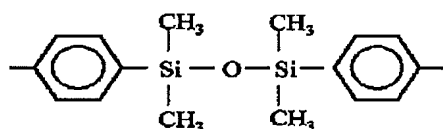
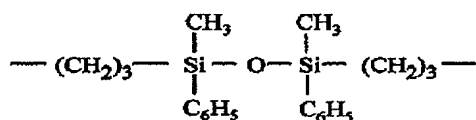
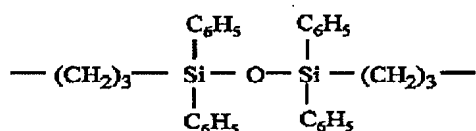
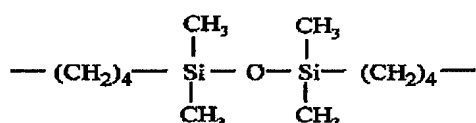
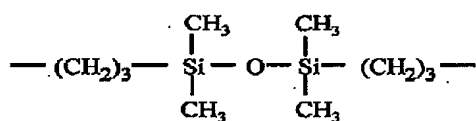
[0014] Moreover, Y of a formula (2) is [Formula 6].



(式中A:  $-\text{CH}_2-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{SO}_2-$ ,  $-\text{CO}-$ ,  
 $-\text{NHCO}-$ ,  $-\text{C}(\text{CF}_3)_2-$ )

\*\*\*\*\* -- although -- it is not limited to these.

[0015] Furthermore, Z of a formula (2) is [Formula 7].



\*\*\*\*\* -- although -- it is not limited to these.

[0016] Although Z of a formula (2) is used to a substrate like a silicon wafer when adhesion is required, it can be used to 40-mol [ a maximum of ] % about the operating rate b. If 40-mol % is exceeded, the solubility of resin will fall extremely, even if it uses the pattern formation approach which is this invention, Society for Cutting Up Men is generated and pattern processing cannot be performed. In addition, in use of these X, Y, and Z, it does not matter even if it is one kind, respectively and is two or more kinds of mixture.

[0017] In the alkaline water solution which is a developer of this invention, in order [ which receives Society for Cutting Up Men which exists in the base of a pattern pars basilaris ossis occipitalis, and the interface of resin ] to be smeared, to raise a sex and

to carry out dissolution removal, it is important to contain the anion mold surfactant expressed with a formula (1).

[0018] As a technique which adds a surfactant in an alkaline water solution, it is shown in JP,3-26380,B, JP,4-55504,B, JP,5-40902,B, JP,6-3549,B, and JP,1-72155,A, for example. However, even if it applies the alkaline developer which added the surface active agent as shown in these to the positive type photopolymer which used the polyamide of this invention as base resin, the effectiveness over good workability is small.

[0019] However, when the alkaline developer containing the anion mold surfactant expressed with the formula (1) of this invention is used, Society for Cutting Up Men in a pattern pars basilaris ossis occipitalis is lost, and resolution improves as a result. As an anion mold surface active agent shown in a formula (1), although dodecyl diphenyl ether disulfon acid sodium salt, dodecyl diphenyl ether disulfon acid ammonium salt, a dodecyl diphenyl ether disulfon acid dimethylammonium salt, a dodecyl diphenyl ether disulfon acid trimethylammonium salt, dodecyl diphenyl ether disulfon acid triethyl ammonium salt, a dodecyl diphenyl ether disulfon acid tetramethylammonium salt, etc. are mentioned, it is not limited to these.

[0020] As for the content of the anionic surfactant in the alkaline water solution which is a developer of this invention, it is desirable in a total alkali nature water solution that it is 0.1 – 10 % of the weight. If it is less than 0.1 % of the weight, it will become easy to generate Society for Cutting Up Men, if 10 % of the weight is exceeded conversely, the alkali concentration of a developer will be reduced, and sensibility will fall.

[0021] Furthermore, it is important for the alkaline water solution which is a developer of this invention to make the chlorine of ultralow volume contain. Although there is JP,4-204454,A as a technique about the alkaline water solution which added the anion mold surfactant, if the alkaline developer containing an anion mold surfactant as shown in these is applied to the positive type photopolymer which used the polyamide of this invention as base resin, even if the pattern without Society for Cutting Up Men is obtained, needing [ the amount of film decreases of resin increases and ]-at time of development, thickness may not be obtained. This is because such an anion mold surfactant of structure has the structure where the compatibility and the permeability over alkali fusibility resin including the polyamide resin of this invention are very high, so it has the capacity to also make the resin of an unexposed part fully dissolve.

[0022] Then, as a result of performing various examination, it found out that it was effective in the ability to stop the amount of film decreases of the unexposed part

after development by making the chlorine of ultralow volume contain in the alkali water solution containing an anion mold surfactant, maintaining good workability without Society for Cutting Up Men. As for the level of chlorine in a total alkali nature water solution, it is desirable that it is 2–200 ppm. When the level of chlorine is less than 2 ppm, it becomes difficult for the amount of film decreases after development to increase, and to obtain desired thickness, since chlorine will become easy to remain after development if [ than 200 ppm ] more, aluminum wiring in a semiconductor device corrodes, and dependability falls.

[0023] The alkaline water solution of this invention can also add the compound of calcium, strontium, and barium, in order to raise the contrast of the resin pattern generated after development. The contrast enhancing effect by these metallic compounds is produced when metallic compounds insolubilize the paint film of resin strongly. As an example of these metallic compounds, although inorganic [ , such as basic compounds, such as a calcium oxide, a calcium hydroxide, a strontium oxide, a strontium hydroxide, barium oxide, and a barium hydroxide, a calcium nitrate, calcium acetate, a strontium nitrate, strontium acetate, a barium nitrate, and barium acetate, ] thru/or organic salt can be mentioned, it cannot be overemphasized that it is not what is limited to the above compound. Moreover, although the content of these metallic compounds changes with classes of metal to be used, 0.1 ppm or more its 1 ppm or less of the whole developer are desirable as these metal simple substance. In the case of less than 0.1 ppm, there are too few contents of metallic compounds and the effectiveness of contrast enhancement is not acquired. Conversely, if [ than 1 ppm ] more, with an unexposed part, the solubility of the exposure section will also fall to coincidence remarkably, sensibility will fall, and resolution will also become low.

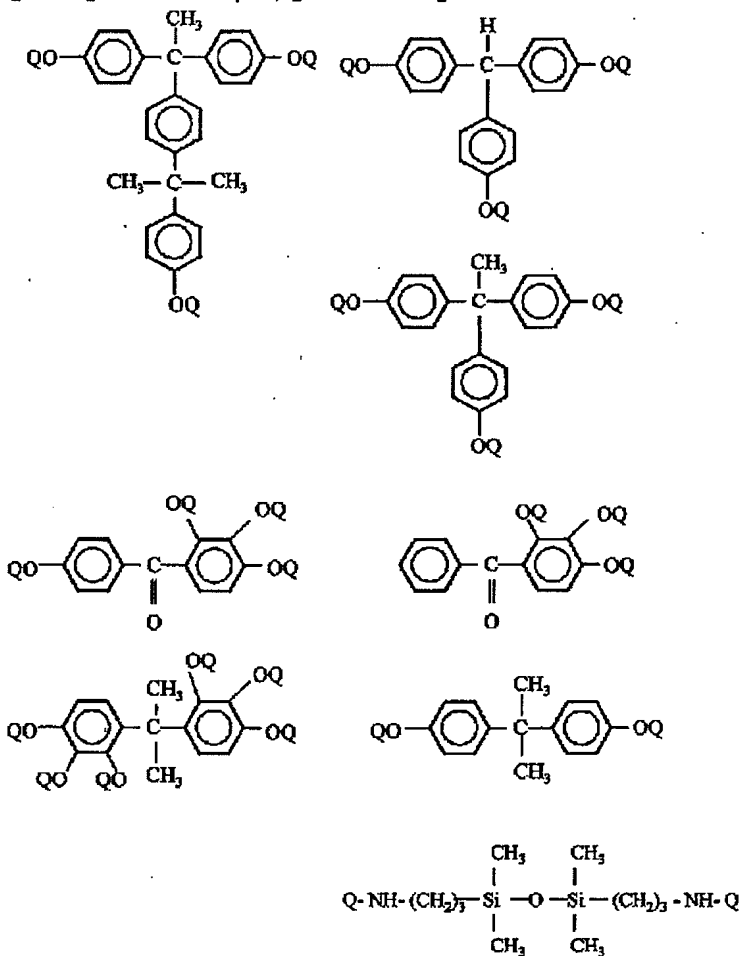
[0024] As for the alkaline water solution of this invention, it is indispensable that it is the water solution which carries out dissolution removal of the alkali fusibility polymer, and dissolved the alkali compound. As an alkali compound, it is \*\*\*\*\* which quarternary ammonium salt, such as alcoholic amines, such as tertiary amines, such as secondary amines, such as primary amines, such as inorganic alkali, such as a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a specific silicate, specific metasilicate, and aqueous ammonia, ethylamine, and n propylamine, diethylamine, and G n propylamine, triethylamine, and methyl diethylamine, dimethylethanolamine, and triethanolamine, tetramethylammonium hydroxide, and tetraethylammonium hydroxide, etc. mentions, for example.

[0025] Although the photopolymer constituent used for this invention uses a polyamide, a diazo quinone compound, and a solvent as a principal component, it may

add a polyamide acid if needed. Since the polyamide acid has the carboxyl group, its solubility increases and shortening of developing time of it is attained.

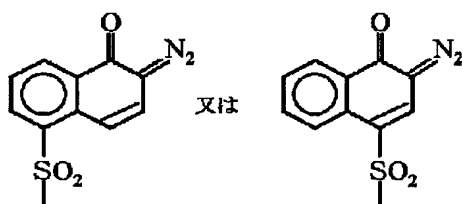
[0026] The diazo quinone used by this invention is a compound which has 1 and 2-benzoquinone diazido or 1, and 2-naphthoquinonediazide structure, and is the well-known matter by the United States patent official report No. 2,772,972, No. 2,797,213, No. 3,669,658, etc.

[0027] For example, [Formula 8]

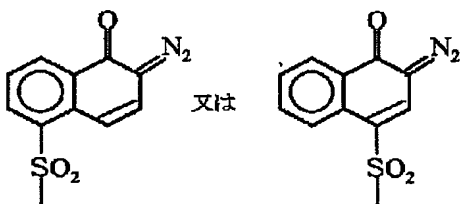


[Formula 9]

(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、



を意味する。)

\*\* can be mentioned.

[0028] The pattern production approach applies a positive type photopolymer constituent to a suitable base material, for example, a silicon wafer, a ceramic, an aluminum substrate, etc. first. The method of application is performed by rotation spreading which used the spinner, spraying spreading using a spray coater, immersion, printing, roll coating, etc. Next, a paint film is dried at the temperature of about 60–180 degrees C. Although there are oven, infrared oven, a heating plate, etc. as a drying method, an effectiveness side and temperature control carry out, and a heating plate is desirable from \*\*\*\*\*. When drying by this heating plate, it is desirable to dry at 80–130 degrees C. Less than 80 degrees C of desiccation are insufficient, and it is not desirable. Moreover, if 130 degrees C is exceeded, since desiccation becomes excessive, it is not desirable. 2 – 4 minutes is more desirable at 100–120 degrees C.

[0029] Next, chemical rays are used for a desired pattern configuration, and an optical exposure is carried out. As chemical rays, although an X-ray, an electron ray, ultraviolet rays, a visible ray, etc. can be used, a thing with a wavelength of 200–500nm is especially desirable. In order to obtain the pattern of high resolution more, it is more desirable to use g line stepper using i line stepper using the wavelength of 365nm or the wavelength of 436nm.

[0030] Hereafter, an example explains this invention concretely.

<<example 1>>

\* 0.8 mols of synthetic terephthalic acids, 0.2 mols of isophthalic acid, 1-hydroxy of a

polyamide – 360.4g (0.9 mols) of dicarboxylic acid derivatives, hexafluoro which two mols of 1, 2, and 3-benzotriazols were made to react, and were obtained – 2 and 2-screw (3-amino-4-hydroxyphenyl) Propane 366.3g (1.0 mols) is put into the separable flask of a thermometer, an agitator, raw material input port, and 4 openings equipped with desiccation nitrogen gas installation tubing, and 3000g of N-methyl-2-pyrrolidones was added, and it was made to dissolve. It was made to react at 75 degrees C for 12 hours using an oil bath after that. After carrying out the \*\* collection of an injection and the precipitate to the solution of water / methanol =3/1 and washing the reaction mixture after filtering a reaction mixture enough with water, it dried under the vacuum, and it was shown by the general formula (1), and the polyamide (A-1) which X becomes by the following formula X-1, and Y becomes from a= 100 and b= 0 by the following type Y-1 and Y-2 was obtained.

[0031] \* After dissolving 20g (Q-1) of diazo quinone compounds which have the structure of polyamide (A-1) 100g in which the positive type photopolymer constituent carried out production composition, and the following type in 200g of N-methyl-2-pyrrolidones, it filtered with the 0.2-micrometer Teflon filter, and the photopolymer constituent was obtained.

[0032] \* After using the spin coater and applying the positive type photopolymer constituent of \*\*\*\*\* on a silicon wafer, it was dried at 120 degrees C with the hot plate for 4 minutes, and the paint film of about 5 micrometers of thickness was obtained. 436nm light was irradiated two times 50 to 500 mJ/cm by g line stepper at this paint film through the mask (test chart No.1: -- a remnants pattern with a width of face of 0.88-50.0 micrometers -- and it extracts and the pattern is drawn) by Toppan Printing Co., Ltd. After carrying out dissolution removal of the exposure section with a paddle method for 60 seconds using the developer which consists obtained \*\*\*\* of the tetramethylammonium hydroxide 1.35 weight section, the deionized water 97.45 weight section, the surfactant (S-1) 1.20 weight section that has the structure of the following type, and 5 ppm of the levels of chlorine, the rinse was carried out for 10 seconds by deionized water. Consequently, it has checked that the pattern without Society for Cutting Up Men was fabricated in the resolution of 4 micrometers from the part irradiated by light exposure 150 mJ/cm<sup>2</sup> (sensibility is 150 mJ/cm<sup>2</sup>). The rate of film decrease at this time (thickness x100(%) before the thickness decrement / development by development; the one where this value is smaller is desirable) showed 11.7% and a good value.

[0033] \* After applying and exposing the above-mentioned positive type photopolymer using the simulation component wafer which equipped the reliability



evaluation front face of a semiconductor device with aluminum circuit so that 5 micrometers of last may come, last BEKU of the pattern processing was performed and carried out using the above-mentioned developer. It divided for every chip size after that, and after using and mounting a conductive paste on the leadframe for 16pinDIP(s) (Dual Inline Package), it cast with the epoxy resin for the semi-conductor closures (the Sumitomo Bakelite Co., Ltd. make, EME-6300H), and 16pinDIP(s) were obtained. After processing these packages on condition that humidity 85 degrees C / 85% and making it a 260-degree C solder bath tub with \*\* during 10 seconds, an elevated temperature and highly humid pressure cooker processing (125 degrees C, 2.3atm, 100%RH) were performed, and poor opening of aluminum circuit was checked.

[0034] <<example 2>> In composition of the polyamide in an example 1 instead of 0.8 mols of terephthalic acids, and 0.2 mols of isophthalic acid It replaced with diphenyl ether -4 and 1.0 mols of 4'-dicarboxylic acid, and was shown by the general formula (1), and the polyamide (A-2) which X becomes by the following formula X-1, and Y becomes from a= 100 and b= 0 by the following formula Y-3 was compounded, the addition of each component was changed as shown in Table 1, and the photopolymer constituent was obtained similarly. Furthermore, after going by the same conditions as an example 1 to a spin coat and prebaking exposure, negatives were similarly developed on them using the developer which consists of the tetramethylammonium hydroxide 1.42 weight section, the pure-water 93.78 weight section, the surfactant (S-1) 4.80 weight section, and 23 ppm of the levels of chlorine.

[0035] <<example 3>> It sets to composition of the polyamide in an example 1, and is hexafluoro. - A 2 and 2'-bis(3-amino-4-hydroxyphenyl) propane is reduced to 348.0g (0.95 mols). It is 1 and 3-screw (3-aminopropyl) to instead of. - 1, 1, 3, and 3-tetramethyl disiloxane 12.4g (0.05 mols) is added. It was shown by the general formula (1) and the polyamide (A-3) which X becomes [ the following type Y-1 and Y-2, and Z ] by the following formula X-1, and Y becomes from a= 95 and b= 5 by the following formula Z-1 was compounded, the addition of each component was changed as shown in Table 1, and the photopolymer constituent was obtained similarly. Furthermore, after going by the same conditions as an example 1 to a spin coat and prebaking exposure, negatives were similarly developed on them using the developer which consists of the tetramethylammonium hydroxide 1.30 weight section, the pure-water 97.90 weight section, the surfactant (S-1) 0.80 weight section, and 8 ppm of the levels of chlorine.

[0036] <<example 4>> After going by the still more nearly same conditions as an example 1 to a spin coat and prebaking exposure using the positive type photopolymer

constituent in an example 1, negatives were similarly developed using the developer which consists of the tetramethylammonium hydroxide 1.35 weight section, the pure-water 97.65 weight section, the surfactant (S-2) 1.00 weight section that has the structure of the following type, and 93 ppm of the levels of chlorine.

[0037] <<example 5>> After going by the still more nearly same conditions as an example 1 to a spin coat and prebaking exposure using the positive type photopolymer constituent in an example 1, negatives were similarly developed using the developer which consists of the tetramethylammonium hydroxide 1.38 weight section, the pure-water 97.37 weight section, the surfactant (S-1) 1.25 weight section that has the structure of the following type, and 147 ppm of the levels of chlorine.

[0038] <<example 6>> After going by the still more nearly same conditions as an example 1 to a spin coat and prebaking exposure using the positive type photopolymer constituent in an example 1, negatives were similarly developed using the developer which consists of the tetramethylammonium hydroxide 1.35 weight section, the pure-water 97.45 weight section, the surfactant (S-1) 1.20 weight section that has the structure of the following type, and 3 ppm of the levels of chlorine.

[0039] <<example 7>> In production of the positive type photopolymer constituent in an example 2, (Q-2) was used instead of the diazo quinone compound (Q-1), the addition of each component was changed as shown in Table 1, and the photopolymer constituent was obtained similarly. Furthermore, after going by the same conditions as an example 1 to a spin coat and prebaking exposure, on them, negatives were similarly developed using the developer which consists of the tetramethylammonium hydroxide 1.40 weight section, the pure-water 97.30 weight section, the surfactant (S-1) 1.30 weight section, and 5 ppm of the levels of chlorine.

[0040] Example of <<comparison 1>> In preparation of the developer in an example 1, it changed into what does not contain the surfactant (S-1) only by the tetramethylammonium hydroxide 1.35 weight section and the pure-water 98.65 weight section, and also the same evaluation as an example 1 was performed.

[0041] Example of <<comparison 2>> In preparation of the developer in an example 2, it changed into the developer which consists of the tetramethylammonium hydroxide 1.42 weight section, the pure-water 85.58 weight section, the surfactant (S-1) 13.00 weight section, and 64 ppm of the levels of chlorine, and also the same evaluation as an example 2 was performed.

[0042] Example of <<comparison 3>> In preparation of the developer in an example 4, it changed into the developer which consists of the tetramethylammonium hydroxide 1.35 weight section, the pure-water 98.60 weight section, the surfactant (S-2) 0.05

weight section, and 5 ppm of the levels of chlorine, and also the same evaluation as an example 4 was performed.

[0043] Example of <<comparison 4>> In preparation of the developer in an example 1, it changed into the tetramethylammonium hydroxide 1.50 weight section, the pure-water 97.30 weight section, and the developer that consists of the 1.20 (S-3) weight sections and 16 ppm of the levels of chlorine instead of a surfactant (S-1), and also the same evaluation as an example 1 was performed.

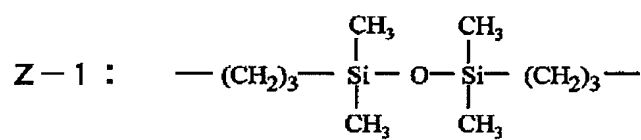
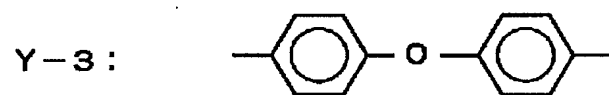
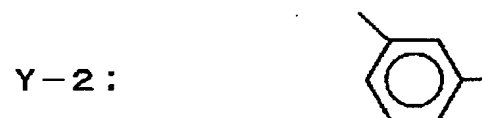
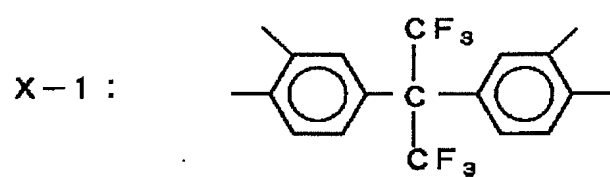
[0044] Example of <<comparison 5>> In preparation of the developer in an example 1, it changed into the tetramethylammonium hydroxide 1.35 weight section, the pure-water 96.65 weight section, and the developer that consists of the 2.00 (S-4) weight sections and 121 ppm of the levels of chlorine instead of a surfactant (S-1), and also the same evaluation as an example 1 was performed.

[0045] Example of <<comparison 6>> In preparation of the developer in an example 1, it changed into the developer which consists of the tetramethylammonium hydroxide 1.39 weight section, the pure-water 97.41 weight section, the surfactant (S-1) 1.20 weight section, and 0.5 ppm of the levels of chlorine, and also the same evaluation as an example 1 was performed.

[0046] Example of <<comparison 7>> In preparation of the developer in an example 1, it changed into the developer which consists of the tetramethylammonium hydroxide 1.40 weight section, the pure-water 97.30 weight section, the surfactant (S-1) 3.00 weight section, and 813 ppm of the levels of chlorine, and also the same evaluation as an example 1 was performed.

[0047]

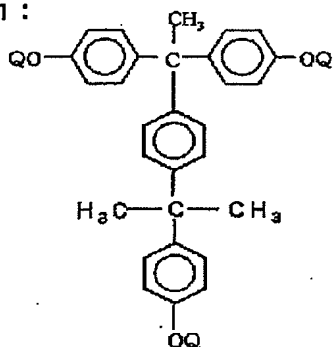
[Formula 10]



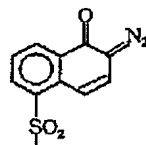
[0048]

[Formula 11]

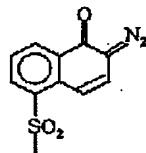
Q-1:



(式中Qは水素原子又は

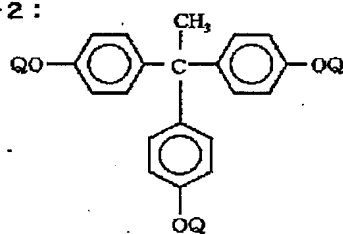


を示し、Q全体の内70%が

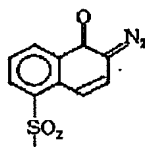


である。)

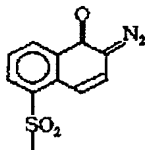
Q-2:



(式中Qは水素原子又は



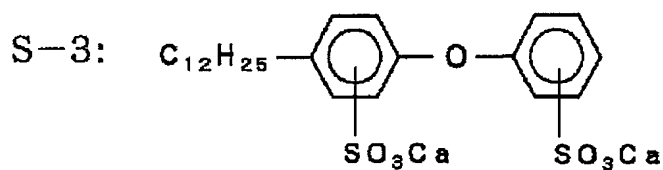
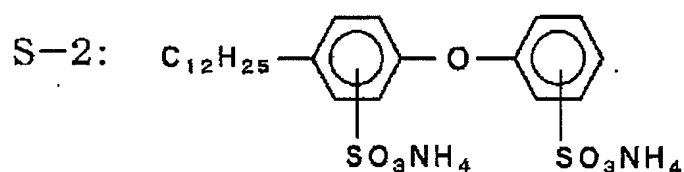
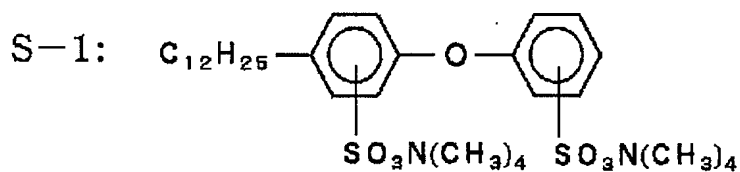
を示し、Q全体の内65%が



である。)

[0049]

[Formula 12]



[0050] The result of an example and the example of a comparison is shown in Table 1.

[Table 1]

表1

|     |   | 7Aカリ可溶性ホリマー<br>100g |         | 感光剤 |          | テトラメチルアンモニウム<br>トリフェニルホスホニウム |     | 界面活性剤 |           | 塩濃度<br>ppm | 現像後の<br>スカムの<br>有無 | 解像度<br>μm | 感度<br>mJ/cm <sup>2</sup> | 膜減り<br>率<br>% | 半導体装置の信頼性<br>(不良数/20パッケージ) |  |
|-----|---|---------------------|---------|-----|----------|------------------------------|-----|-------|-----------|------------|--------------------|-----------|--------------------------|---------------|----------------------------|--|
|     |   |                     |         | 種類  | 添加量<br>g | 比重<br>重量%                    | 種類  | 重量%   | PCT 500hr |            |                    |           |                          |               | PCT 1000hr                 |  |
|     |   | アジ                  | 酸       |     |          |                              |     |       |           |            |                    |           |                          |               |                            |  |
| 実施例 | 1 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-1 | 1.20  | 5         | 無し         | 4                  | 150       | 11.7                     | 0/20          | 0/20                       |  |
|     | 2 | X-1                 | Y-3     | Q-1 | 19       | 1.42                         | S-1 | 4.80  | 23        | 無し         | 5                  | 220       | 9.8                      | 0/20          | 0/20                       |  |
|     | 3 | X-1/Z-1<br>95/5モル%  | Y-1,Y-2 | Q-1 | 18       | 1.30                         | S-1 | 0.80  | 8         | 無し         | 5                  | 190       | 10.0                     | 0/20          | 0/20                       |  |
|     | 4 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-2 | 1.00  | 93        | 無し         | 3                  | 170       | 12.1                     | 0/20          | 0/20                       |  |
|     | 5 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.38                         | S-1 | 1.25  | 147       | 無し         | 4                  | 150       | 10.6                     | 0/20          | 0/20                       |  |
|     | 6 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-1 | 1.20  | 3         | 無し         | 4                  | 150       | 11.5                     | 0/20          | 0/20                       |  |
|     | 7 | X-1                 | Y-3     | Q-2 | 22       | 1.40                         | S-1 | 1.30  | 5         | 無し         | 4                  | 190       | 10.5                     | 0/20          | 0/20                       |  |
| 比較例 | 1 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-1 | 0.00  | 5         | 有り         | 15                 | 340       | 10.3                     | 0/20          | 0/20                       |  |
|     | 2 | X-1                 | Y-3     | Q-1 | 19       | 1.42                         | S-1 | 13.00 | 64        | 無し         | 6                  | 540       | 7.9                      | 0/20          | 0/20                       |  |
|     | 3 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-2 | 0.05  | 5         | 有り         | 10                 | 140       | 14.9                     | 0/20          | 0/20                       |  |
|     | 4 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.50                         | S-3 | 1.20  | 18        | —          | 現像出来ず              |           | —                        | —             | —                          |  |
|     | 5 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.35                         | S-4 | 2.00  | 121       | 有り         | 10                 | 160       | 9.8                      | 0/20          | 0/20                       |  |
|     | 6 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.39                         | S-1 | 1.20  | 0.5       | 無し         | 4                  | 100       | 23.3                     | 0/20          | 0/20                       |  |
|     | 7 | X-1                 | Y-1,Y-2 | Q-1 | 20       | 1.40                         | S-1 | 3.00  | 813       | 無し         | 4                  | 170       | 8.8                      | 0/20          | 2/20                       |  |

[0051]

[Effect of the Invention] If a positive type photopolymer constituent is developed in an anionic surface active agent and the alkali water solution containing the chlorine of ultralow volume, sensibility and the rate of film decrease are not only excellent, but the development remainder (Society for Cutting Up Men) will not generate this invention. Therefore, the pattern formation of high resolution of the positive type photopolymer constituent which consists of a polyamide and a quinone diazide compound becomes very possible.

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[Translation done.]